THE EFFECT OF OXIDATION TREATMENT OF MWCNT ON THE PROPERTIES OF PDMS NANOCOMPOSITE

by

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Norkhairunnisa Binti Mazlan
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LIST OF ABBREVIATIONS

AlBN	: Azobisisobutyronitrile
BF_3	: Boron trifluoride
CVD	: Chemical Vapor Deposition
DMA	: Dynamic mechanical analysis
DTA	: Dynamic thermal analysis
DWCNT-NH_2	: Amino functionalized Double walled Carbon Nanotube
EDX	: Energy Dispersive X-ray
FE-SEM	: Field emission scanning electron microscope
FTIR	: Fourier transform infrared
HCl	: Hydrochloric acid
HF	: Hydrogen fluoride
HNO_3	: Nitric acid
HSMA	: Hydrolyzed Poly(styrene-co-maleic anhydride)
HSO_4^-	: Bisulfate ion
H_2O_2	: Hydrogen peroxide
H_2SO_4	: Sulphuric acid
H_3O^+	: Hydronium ion
iPP	: Isotactic polypropylene
KBr	: Potassium bromide
$KmnO_4$	: Potassium permanganate
MMA	: Methyl methacrylate
MWCNT-NH_2	: Amino functionalized Multi walled Carbon Nanotube
Nmwcnt	: MWCNT oxidized in nitric acid
nsMWCNT	: MWCNT oxidized in acid mixture
NaClO	: Sodium hypochlorite

NO_2^+	: Nitronium ion
NaOH	: Sodium hydroxide
OsO_4	: Osmium tetroxide
PDMS	: Polydimethylsiloxane
PMAS	: Poly(styrene-co-maleic anhydride)-block-polystyrene
PMMA	: Polymethylmethacrylate
PP	: Polypropylene
PS	: Polystyrene
PTFE	: Polytetrafluoroethylene
PU	: Polyurethane
P3HT	: Poly(3-hexylthiophene)
RBM	: Radial breathing mode
SEM	: Scanning electron microscope
SLS	: Sodium lauryl sulfonate
TEM	: Transmission Electron Microscope
TGA	: Thermogravimetric analysis
TLCP	: Thermotropic liquid crystalline polymer
UV-vis	: Ultraviolet visible
XRD	: X-ray diffraction
XPS	: X-ray photoelectron spectroscopy

LIST OF SYMBOLS

π	: Pie
σ	: Sigma
%	: Percent
at%	: Atomic percent
wt%	: Weight percent
vol%	: Volume percent
T_g	: Glass transition temperature
E’	: Storage modulus
E’’	: Loss modulus
l	: Length
d	: Diameter
D	: Diameter of sphere
k_f	: Thermal conductivity of filler
k_m	: Thermal conductivity of matrix
ρ_s	: Density of sample
m_s	: Mass of sample
v_s	: Volume of sample
Ar^+	: Argon ion
t	: Sample thickness
Ω	: Electrical resistance
A	: Area
ρ	: Density
I_D	: Intensity of D band
I_G	: Intensity of G band
δ	: Tan delta (loss factor)

KESAN RAWATAN PENGOKSIDAAN MWCNT KE ATAS SIFAT-SIFAT NANOKOMPOSIT PDMS

ABSTRAK

MWCNT mempunyai sifat elektrikal yang unik, kekonduksian terma yang lebih tinggi daripada berlian, and sifat mekanikal yang baik di mana kekuatan dan kekakuan melebihi bahan lain yang sedia ada. Walaubagaimanapun, kurangnya serakan dan pengikatan antaramuka antara MWCNT dan matrik polimer memberi satu cabaran dalam menghasilkan nanokomposit yang mempunyai sifat yang bagus. Rawatan pengoksidaan dilakukan ke atas MWCNT bagi menambahbaikkan serakan dan pengikatan antaramuka di antara nanotiub dengan PDMS. Kefungsian pengoksidaan MWCNT dihasilkan melalui pengoksidaan menggunakan sama ada asid tunggal (HNO_3) atau gabungan asid (HNO_3/H_2SO_4) pada nisbah 3:1. Rawatan ini dilakukan pada tempoh masa (3 dan 6 jam) dan suhu (80°C dan 140°C) rawatan yang berbeza. Analisa FTIR dan XPS menunjukkan kehadiran pelbagai kumpulan berfungsi oksigen seperti C-O, C=O dan COOH. Nisbah kandungan O/C meningkat dari 0.17 bagi MWCNT yang tidak dirawat, kepada 0.56 bagi MWCNT yang teroksida. Pentitratan asid bes menunjukkan peningkatan kandungan kumpulan asid sebanyak 159%. Kesan pengoksidaan memberi kesan yang lebih ketara apabila suhu rawatan ditingkatkan kepada 140°C selama 6 jam sehinggakan nisbah I_D/I_G didapati meningkat dari 0.19 kepada 0.83 serta terdapat penurunan dalam kestabilan terma. Kewujudan kumpulan berfungsi menyebabkan pembentukan lapisan elektrik berganda pada permukaan MWCNT, lalu menghasilkan serakan yang baik di dalam air. Lapisan ini juga mampu mengatasi daya tarikan van der Waals antara nanotiub, lalu menurunkan saiz gumpalan. Selain itu, kecacatan ke atas MWCNT dan kewujudan kumpulan pemangkin dapat dilihat melalui TEM. Bagi PDMS terisi

dengan MWCNT yang dirawat dengan HNO_3 pada 80°C untuk 3 dan 6 jam, didapati kekuatan tensil meningkat kepada 5.06 MPa, manakala kekonduksian terma dan elektrik masing-masing meningkat sedikit kira-kira 24% dan 42% dibandingkan dengan nanokomposit MWCNT/PDMS yang tidak dirawat. Walaubagaimanapun bagi PDMS terisi dengan MWCNT yang dirawat pada suhu 80°C selama 6 jam di dalam gabungan asid, terdapat sedikit penurunan dalam sifat terma dan elektrikal, masing-masing kepada 0.19 W.mK dan -4.62 Log/Scm^{-1}. Penurunan lebih ketara bagi PDMS terisi MWCNT yang dirawat pada suhu 140°C selama 6 jam kerana terdapat penurunan nilai T_g sebanyak 9°C berbanding PDMS terisi dengan MWCNT yang telah dioksidakan pada 80°C selama 6 jam. Pengoksidaan yang terlampau ke atas MWCNT mengurangkan keupayaannya untuk membentuk ikatan antaramuka yang baik dengan matrik PDMS. Oleh itu, MWCNT jenis ini sesuai digunakan untuk meningkatkan sifat keplastikan pada matrix polimer.

THE EFFECT OF OXIDATION TREATMENT OF MWCNT ON THE PROPERTIES OF PDMS NANOCOMPOSITE

ABSTRACT

MWCNT have a unique electrical properties, thermal conductivity which is higher than diamond and a good mechanical properties where strength and stiffness exceed any other current materials However, poor dispersibility and interfacial adhesion of MWCNT in polymer matrix presents a considerable challenge in developing nanocomposite with good properties. Oxidation treatment was done on MWCNT as to improve the dispersion and interfacial adhesion between the nanotubes and PDMS. The oxidation treatments of MWCNT were carried out by oxidizing using either single acid (HNO_3) or mixture of acids (HNO_3/H_2SO_4) at 3:1 ratio. The treatments were done for different period of time (3 and 6 hours) and temperature (80°C and 140°C). FTIR and XPS analysis showed the presence of various functional groups such as C-O, C=O and COOH. The O/C ratio increased from 0.17 for untreated MWCNT to 0.56 for oxidized MWCNT. Acid bes titration showed increase in concentration of acid groups about 159%. The oxidation affects the tubes more significantly when the temperature and time increased to 140°C and 6 hours respectively as the I_D/I_G ratio increased from 0.19 to 0.83 and reduction in thermal stability. The presence of functional groups formed electrical double layer on the MWCNT surface and thus, gave good dispersibility in water. This layer also overcome the strong van der Waals force within the nanotubes and reduced agglomeration. The presence of defects and catalysts were also observed by TEM. For PDMS filled with MWCNT oxidized in HNO_3 at 80°C for 3 and 6 hours, the tensile strength increased to 5.06 MPa, while thermal and electrical conductivity slightly increased for approximately to 24% and 42%, respectively over the untreated

MWCNT/PDMS nanocomposites. However, for PDMS filled with MWCNT oxidized at 80°C for 6 hours in acid mixture, the thermal and electrical conductivities were slightly decreased to 0.19 W/mK and -4.62 Log/Scm^{-1}. Decrease in properties was more significant for PDMS filled with MWCNT oxidized at 140°C for 6 hours as the T_g value decreased for 9°C compared PDMS reinforced with MWCNT oxidized at 80°C for 6 hours, in which its T_g was approximately -35°C. Aggressive oxidation treatment reduces the capability of MWCNT to form good interfacial interaction with the PDMS matrix. However, this type of MCWNT was suitable to be used to increase the plasticity of the polymer matrix.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Nanostructured materials play an important role in the past decade due to their wide range of potential applications in many areas such as in the field of aerospace (Taczak, 2006), actuators (Ashrafi *et al.*, 2006), biomedical (Ji *et al.*, 2010), electronics (Wang *et al.*, 2010), etc. One of the promising nanostructured materials is Multi-walled Carbon Nanotube (MWCNT) which can be utilized in various applications as reinforcing fillers especially in the field of polymer-based composites. High aspect ratio (*l/d*, where *l* is length and *d* is diameter) of CNT facilitates it to form network like structure in the composite. Moreover, its unique electronic properties, high structural flexibility and high mechanical strength make it stiffer and stronger materials than other potential materials such as graphene, diamond, carbon black, etc. Thus, various types of polymer have been embedded with CNT with a desire to fabricate new advanced materials as to enhance the composite properties.

Few reviews focusing on elastomer nanocomposites have been reported in recent years. Likozar and Major (2010), overviewed the distribution of MWCNT in the elastomer rubber matrix and found out that the presence of MWCNT improved the performance of the nanocomposites. In addition, degree of dispersibility and high aspect ratio of CNT affects the thermal conductivity of the elastomer filled MWCNT as investigated by Hong *et al.* (2010). Hikage *et al.*, (2007) analyze elastomer containing different fillers in order to develop a lightweight human phantom with

specific gravity below 1.0. While Bokobza and Kolodziej (2006), examined different level of reinforcement for elastomer contained different fillers.

Polydimethylsiloxane (PDMS) is one of the high performance silicone rubber elastomer with combination of high flexibility of $-[Si-O]_x-$ chain segments with inherent strength of (Si-O) siloxane bonds, excellent thermal stability with slow heat release rates, low viscosity, low surface free energy, low toxicity and less chemical reactivity (Hamdani *et al.* (2009), Chaudhry and Billingham (2001), Mark (2004), Esteves *et al.* (2010)). Due to the high performance of PDMS material it may suitable to be combined with the versatile filler such as MWCNT. As we know, the CNT price in the market is too high. Thus, limit the use and exploration of CNT in research study. However, the CNT price has dropped dramatically over the past several years due to the efforts that focused on realizing mass production of CNT and its application in many field of industries.

Recent articles review on four requirements systems for effective reinforcement as mentioned by Coleman *et al.* (2006). These systems are (i) a large aspect ratio to maximize the load transfer to CNT, (ii) good dispersibility of individual CNT throughout the polymer matrix, (ii) randomness and alignment of CNT, and (iv) interfacial load transfer so as to achieve an efficient load transfer to the CNT network.

However, the as manufactured CNT exists as agglomerates of several hundred micrometers due to extremely high surface energy combined with impurities contamination create an obstacle to most applications. The tube surface not only

attracted to each other by van der Waals force but also due to their extremely high aspect ratio and high flexibilities increase the possibility of entanglements. Highly entangled CNT are difficult to disperse uniformly throughout the matrix. Moreover, agglomeration of CNT could not provide three-dimensional networks which are important in transport properties such as electrical and thermal conductivity. Poor interfacial strength of CNT and matrix in composite may cancel the uniformity of stress distributions and increase the stress concentration in the composite. The stress transfer occurred between matrix and nanotube at interface critically control the mechanical properties of the composites. Therefore, it is necessary to break the van der Waals force so as to get rid the CNT entanglements by shortening the CNT length. Apart from breaking the CNT entanglements, the impurities that might present in the as-prepared CNT were metal catalyst particles, amorphous carbon and other carbonaceous species. Monodispersity and high purity of CNT are essential for it to function as a reinforcing material.

However, there is still huge contrast between the promising potential and reality of using CNT in practical applications on a widespread scale. Up to date, there has not been a study that examine on the effect of different oxidation treatment of MWCNT in PDMS. The main goals of this work were first to functionalize the MWCNT with either HNO_3 or mixture of HNO_3/H_2SO_4 acids and investigated the outcome from the oxidation process. Both HNO_3 and HNO_3/H_2SO_4 acids are choose because they function as strong oxidizing agent and can provide more oxygen functional groups on the nanotube surface. Subsequently, the properties of the PDMS filled with oxidative MWCNT are determined.

1.2 Problem Statement

Due to the strong van der Waals force, high aspect ratio and high flexibility of CNTs, they tends to agglomerates and entangles among the tubes. This led to poor interfacial bonding between CNT and matrix. Therefore, it is necessary to break down the van der Waals force among CNT in order to reduce the entanglement/or agglomerations of the CNT in matrix. The CNT surface can be functionalized either by chemical (Datsyuk *et al.*, 2008) or physical (Wang *et al.*, 2003) treatments. Physical dispersion methods include ball milling, ultrasonication in selected solvent, grinding, and high speed shearing. These methods may disrupt the CNT structure by inducing severe damage on the tube walls. In chemical modification method, the CNT can be functionalized by covalent (Verdejo *et al.*, 2007) or non-covalent treatment (Wang *et al.*, 2008b). Covalent treatment is functionalizing the CNT surface with functional groups, while non-covalent treatment is surrounding or wrapping the CNT with polymer chain. These chemicals method also may give rise to CNT being damaged due to the strong acid treatment. Therefore, as stated above, combination of cutting and functionalization of CNT are good ways to have good dispersion of CNT in polymer matrix. In addition, the oxidation process can create defects on the CNT surface with abundance of functional groups on top of it. Thus, both CNT and matrix can have better interfacial bonding.

In order to improve the processability of CNT in polymer matrix, the CNT length need to be loosen and shorten. At the same time the CNT need to be oxidized as well so as to improve the CNT dispersibility and formed strong interfacial bonding between CNT and polymer matrix. The oxidation process also led to reduction in length of the CNT and affect the size distribution as well.

The raw (as produced) CNT contained many impurities such as metal catalyst and amorphous carbon. Presence of these unwanted materials might reduce the properties of the composite as well. Oxidation process might help in diminish or reduce these unwanted materials.

It is evident from many studies that the presence of oxygenated functional groups on the CNT serves as starting point for binding with the polymer matrix. Besides that, defects created on the CNT surface during the oxidation process can tailor the CNT surface for desired applications. The CNT is more reactive at their tips and on the defects walls, thus enhanced the chemical reactivity.

The oxidation process on CNT need to be controlled in order to obtain CNT with adequate functional groups and optimum CNT length that is sufficient for composite applications to be realized. Datsyuk *et al.* (2008), reviewed on the different chemical oxidation treatment on MWCNT. Hong *et al.* (2007), examined the effects of different oxidative conditions on the properties of MWCNT in PP nanocomposites. Different mechanical and oxidative treatment on CNT in epoxy nanocomposites have been investigated by Li *et al.* (2007). Thus, it can be said that controlling the oxidation process may affect the intrinsic properties of the CNT, as well as the nanocomposite.

1.3 Objectives of the Study

The functionalization of MCWNT is accomplished by oxidative acid treatment. The PDMS was reinforced with oxidized MWCNT. The objectives of this work are:

a) To prepare and investigate the effects of different oxidative acid treatment on MWCNT at different time and temperature treatment.
b) To study different properties between as-received MWCNT and functionalized MWCNT.
c) To compare the properties of the unmodified MWCNT/PDMS nanocomposite with oxidative MWCNT/PDMS nanocomposite.
d) To investigates the interactions between the oxidized MWCNT and PDMS matrix.

1.4 Project Overview

In achieving the objectives, four main experiments were conducted. First and second experiment involved oxidized acid treatment on the MWCNT by HNO_3 or HNO_3/H_2SO_4 at 80°C with different treatment time and constant treatment time with different oxidized processing temperature, respectively. In this experiment, the outcome of the resulting oxidized MWCNT product were characterized so as to understand the effects of the different oxidative treatments. Density, dispersibility of CNT in distilled water, stability and quality of the CNT suspension, electrophoretic mobility of CNT, structural integrity of CNT, thermal stability, functional groups analysis, acid base titration analysis, and morphological analysis of the MWCNT was further investigated using characterization techniques mentioned in chapter three.

Moreover, properties between the as-received MWCNT and oxidized MWCNT were also evaluated.

Next, third and fourth experiments were conducted by embedding the resultant of the oxidized MWCNT from experiment one and three, respectively, in PDMS matrix. The mechanical, thermal, electrical, morphology and swelling properties of the cured unmodified MWCNT/PDMS and oxidative MWCNT/PDMS nanocomposites were identified. Moreover, selected nanocomposite were sent for XPS analysis so as to investigate presence of bonding between the oxidized MWCNT and PDMS matrix.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the review is focus on oxidation process of MWCNT since the aim of this study is to understand the effects of oxidized MWCNT on the PDMS nanocomposites. The purpose on the oxidation study is to understand the effect of functionalization on the nanotubes in hoping that the properties of the treated nanotubes is better than untreated nanotubes. The review focus more on oxidation treatment of MWCNT. Various effects on the oxidation process such as opening the end capped tubes, promoting the functional groups on the tubes surface, cutting the tube length, removal of catalyst in the tubes in or near the end tubes and thermal stability of the oxidative tubes were discussed.

Finally, the review focus on the silicone rubber filled with oxidized MWCNT, on mechanical, thermal and electrical properties of the nanocomposites. Overall, this chapter discussed on oxidation treatment used in this work and its effect on the properties of the MWCNT/ polymer composite.

2.2 Carbon in General

Carbon (C) was the sixth most abundant element exist in the universe. It provides the framework for all living creatures. The element can be found in the form of amorphous carbon, graphite, diamond, carbon 60, carbon nanotubes, buckminsterfullerenes and many more. Moreover, compound of carbon with other elements were also very common.

Carbon is also known to have four electrons in its valence shell. The core electrons is $1s^2$ which is strongly bonded while the other four valence electrons are weakly bonded. Thus, each carbon atom can share electrons up to four different atoms and combine with another carbon atom or other elements. Owing to this fact, carbon can be in the form of various multi-atomic structures with different molecular configurations called allotropes. The allotropes involve hybridization process. Hybridization determined the chemical, physical and configurational properties of the carbon materials.

Figure 2.1 shows the carbon materials with different types of hybridization. sp hybridization can be observed in carbyne, sp^2 hybridization is observed in graphite and sp^3 hybridization is found in diamond (Popov, 2006). There were sp, sp^2 and sp^3 hybridization as shown in Figure 2.1 which related to the carbon atom forming small organic molecules such as adamatane, ovalene and cumulene. Diversification from the organic molecules leads to the formation of the carbon nanofillers such as nanodiamond, fullerene, nanotubes and graphene. More complex unit of carbon can be form such as carbon onions, nanotubes (NT) ropes, MWNT, nanocarbon diamond (NCD) films, carbon fibers and carbon black with bigger structure size of the carbon nanofillers. Carbon nanofillers are defined as a material that built at nanometer scale ranging from fullerenes, carbon nanotubes to nanoporous materials (Endo *et al.*, 2004).

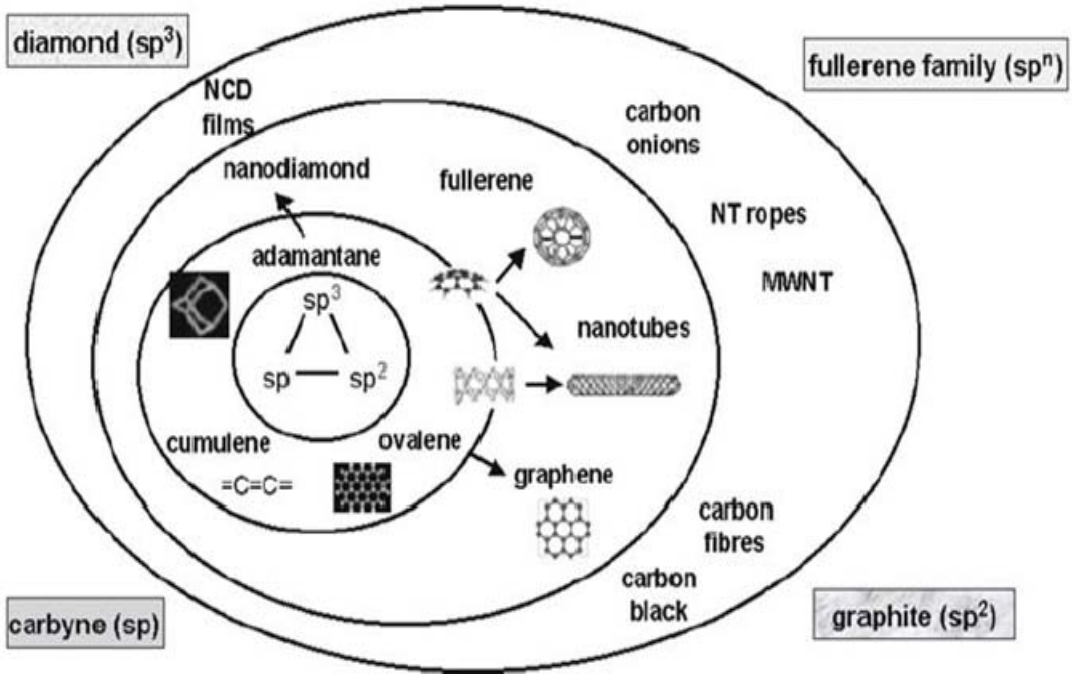

Figure 2.1 Carbon nanoworld based on the different types of hybridization, utilizing the bottom up approach (Popov, 2006).

2.2.1 Carbon Nanotube (CNT)

Carbon Nanotubes (CNTs) were first discovered by Japanese electron microscopist Sumio Ijima in 1991 (Ijima S, 1991). He found a graphitic structure including nanoparticles and nanotubes that had never been observed before (Arben, 2006). Figure 2.2 shows the schematic of individual sheet of graphene and rolled graphene to form CNT. CNT can be thought as a single graphite layer that is rolled up to make a seamless hollow cylinder (Endo *et al.*, 2004). It consists of a variety of diameter in nanosized with many microns in length. CNTs with only one carbon sheet are named single-walled carbon nanotubes (SWCNTs) while CNT with multi layer of graphene rolls are known as Multi-Walled Carbon Nanotubes (MWCNT). Jeykumari and Narayanan (2009) noted that MWCNT usually have diameter of 2 to 100 nm with 2 to 10 nm in internal diameter, while SWCNT have about 0.2 to 2 nm

in diameter. Hayashi *et al.* (2003), shows that the as-produced CNT usually have closed cap and catalyst that may exist at the end cap of the tube where the growth occurs as illustrate in Figure 2.3.

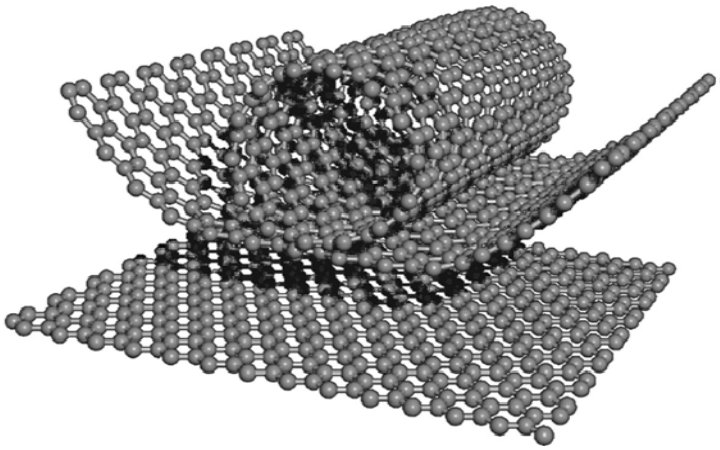

Figure 2.2 Schematic of individual sheet of graphene and rolled graphene in order to form a carbon nanotube (Endo *et al.*, 2004).

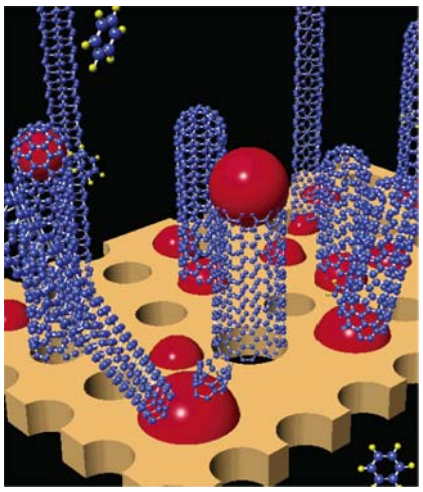

Figure 2.3 Schematic images on the growth of the carbon nanotube. Blue cages indicate the carbon nanotubes. Red balls indicate catalytic particles (Hayashi *et al.*, 2003).

2.2.1.1 Multi-walled Carbon Nanotube (MWCNT)

Figure 2.4 shows that Multi-walled carbon nanotubes (MWCNTs) have several coaxial graphene (Merkoçi, 2006). The early structure was multiwall morphology consist of coaxial cylinders arranged in a “Russian doll” configuration.

Shanmugam and Gedanken (2006) have successfully created MWCNT with different shaped such as bamboo-shaped, straight and twisted MWCNT by pyrolysis process.

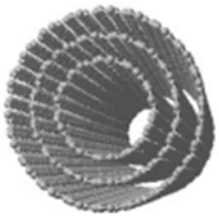

Figure 2.4 Multi walled carbon nanotubes (MWCNT) (Merkoçi, 2006).

According to Meyyapan (2005), when the graphene rolled over to form a CNT, the electrons get confined in particular direction, which insist on the formation of rehybridization. In rehybridization, three σ-bonds went slightly out of plane and the π-bond becomes more delocalized outside of the nanotubes. The three σ-bonds are responsible for the mechanical strength of the CNT while π-bond is accountable to the electronic and thermal properties of the CNT. The π-bonds are also responsible for the interaction between the layers in MWCNT and between SWCNTs in SWCNT bundle (Ruoff *et al.*, 2003).

2.3 CNT Chirality

CNT also was uniquely different from other types of filler. Despite its long tubular structure with hole in the middle, it has different tube chirality (Figure 2.5). According to Harris (2004), the 'zigzag' and 'armchair' refer to the arrangement of the hexagons around the circumference. As for the chiral structure, the hexagons are arranged helically around the tube axis.

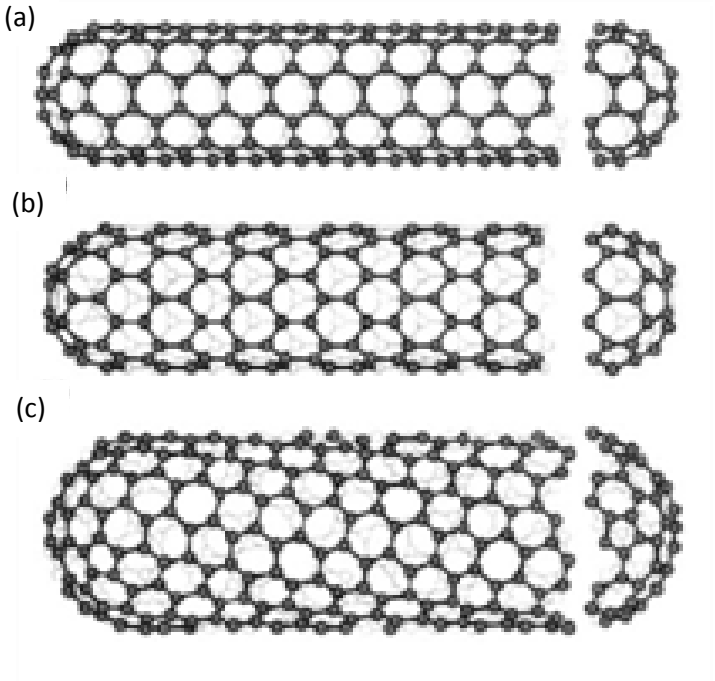

Figure 2.5 Chirality of carbon nanotube (a) armchair (n, m) - (5, 5); (b) zigzag (n, m) – (9, 0); and (c) (n, m) – (10, 5) (Harris, 2004).

2.4 CNT Production

The CNT is manufactured in many different ways and the CNT are produced along with different amount of catalyst impurities and amorphous carbon. There are three main methods used in the synthesis of CNT which are arc-discharge, laser ablation and chemical vapor deposition (CVD) as described by Eichhorn and Stolle (2008).

In arc discharge methods, the MWCNT is produced through arc-vaporization of two graphite rod placed end to end as represented in Figure 2.6. The chamber is filled with inert gas such as helium or argon at low pressure. Arc discharge techniques give the highest amount of catalyst particles while CVD technique was the least (Chaturvedi *et al.*, 2008). Thus this explained the drawback in using arc-discharge method which is more expensive because the need to remove the unwanted

metal catalyst and non-nanotube carbon from the as produced CNT. The presence of impurities and amorphous carbon will affect the mechanical properties of the composites (Schulte *et al.*, 2005).

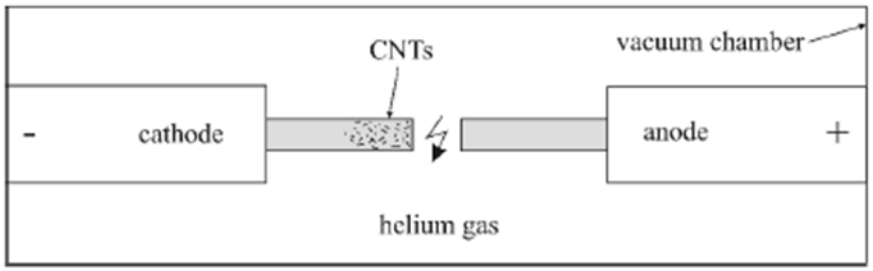

Figure 2.6 CNT production by arc discharge (Eichhorn and Stolle, 2008).

Figure 2.7 shows the production of CNT by laser ablation technique. The laserbeam was directed straight to the graphite target and vaporize it. The vaporized carbon particles move to copper collect vessel with aid by argon flow. This technique produces 70% of CNT by weight and mainly producing CNT with high tubes quality. The disadvantage with this technique is the high cost of operation due to demand of having high-powered laser.

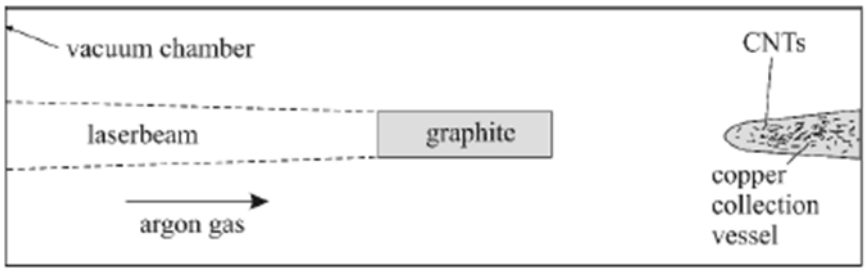

Figure 2.7 CNT production by laser ablation (Eichhorn and Stolle, 2008).

Both arc discharge and laser ablation techniques, are limited in volume sample and relatively high cost in producing the CNT. Thus, the limitations have motivated the the development of gas phase technique in producing CNT such as Chemical Vapor Deposition (CVD). In the CVD method (Figure 2.8), methane gases

was utilize as a source for carbon atoms combined with metal catalyst particles as seeds to support the growth of the nanotubes at relatively low temperatures (500-1000°C). The production of CNT can be up to 100% by weight. The advantage of CVD technique is, simple and favorable technique since the processing technique is cheap with less impurities on CNT.

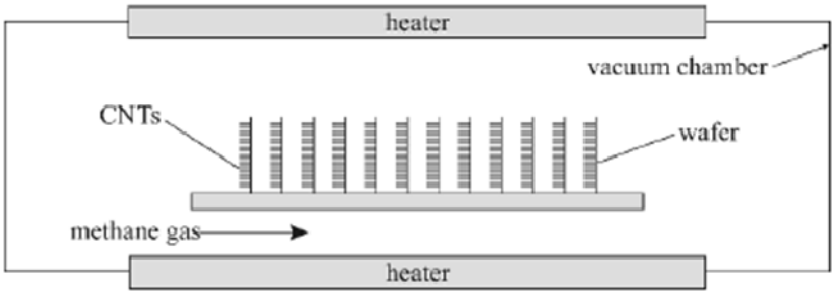

Figure 2.8 CNT production by CVD (Eichhorn and Stolle, 2008).

2.5 Comparisons in Output Analysis between MWCNT and SWCNT

The structure of the MWCNT and SWCNT can be differentiated by observation under electron microscopy and Raman analysis (Valcárcel *et al.*, 2007). Figure 2.9 shows that SWCNT consist of only single wall layer while MWCNT have multiple layers of wall. From electron microscopy, it can be seen that strong interaction between neighboring SWCNT is due to the van der Waals force, which make the SWCNT packed into thick bundle or ropes.

In Raman spectrum, both SWCNT and MWCNT have D and G bands. The D band associates to the disorder graphite while G band refer to the degree of graphitization of the CNT. The difference between SWCNT and MWCNT in Raman analysis lies on the third mode named radial breathing mode (RBM). The intensity of RBM is dependent on the diameter of CNT (Eichhorn and Stolle, 2008). This RBM band which is significantly appear in SWCNT while for MWCNT, the RBM band

appears only if the MWCNT have small diameter in few nanometers (Ando *et al.*, 1999). The RBM signals was near 100-300cm^{-1} which indicate changes in diameter distribution (Seifi *et al.*, 2007).

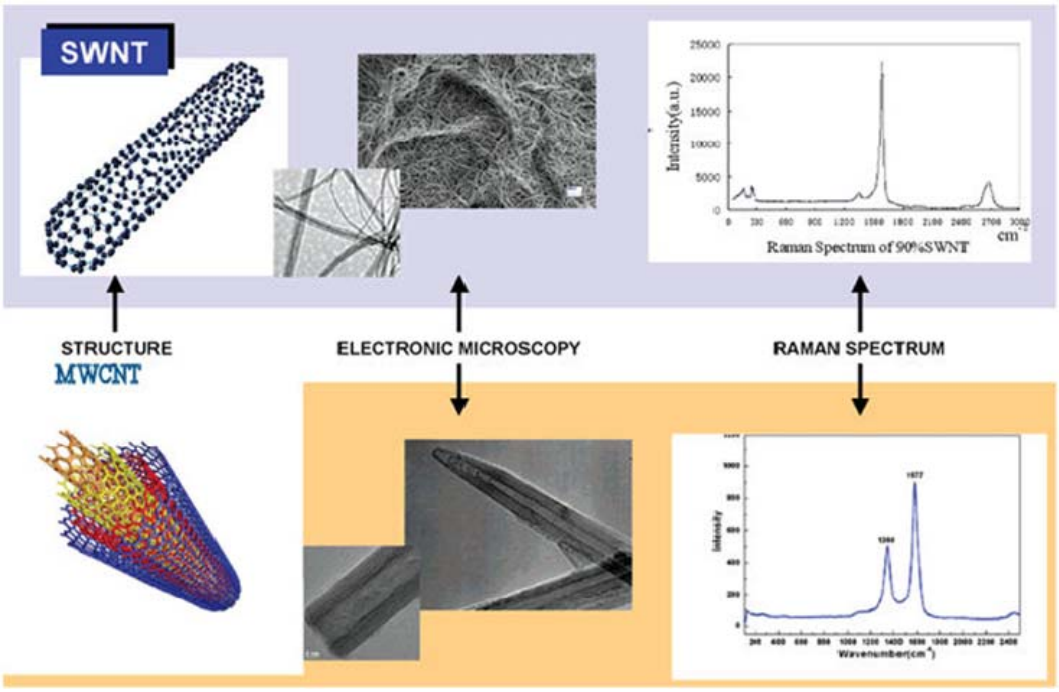

Figure 2.9 Comparison of structures, microscopy images and Raman spectrum between SWCNT and MWCNT (Valcárcel *et al.*, 2007).

2.5.1 MWCNT as Preferred Filler in Composite

There are few reasons on selecting MWCNT as filler in composite rather than SWCNT. It is not only due to the low cost of production but also due to the physical properties of the MWCNT itself. The MWCNT are more rigid than SWCNT because they consist of several rolls of graphene sheet that make it more stable than SWCNT. MWCNT also can act as carbon micro- or nanoparticles. In addition, only low loading of MWCNT is needed in order to achieve percolation threshold. Thus, MWCNT can exhibit excellent mechanical, thermal and electrical properties. Moreover their aspect ratio is as high as 1000, which can induce better interfacial interaction with the polymer matrix (Bikiaris *et al.*, 2008). In order to improve interaction between filler and matrix, CNT might be required to be treated and

functionalized. The SWCNT is not suitable for oxidative treatment. This is because those SWCNTs are so small and hence not protected by outer layers. By creating defects on the SWCNT surface, the tubes will collapse spontaneously due to their instability during the process (Ago and Yamabe, 1999).

2.6 General Properties of CNT

CNT have been intensively studied by most researchers due to the low density of the tubes and offer better mechanical, thermal and electrical properties as reinforcing filler in the composite. The diameter of the tubes can be as small as 0.4nm. The aspect ratio can be very large which are greater than 10^4. CNT have sp^2 bonding which consists of one σ-orbital and two π-orbital are hybridized and take part in covalent bonding. The sp^2 bonds can make the nanotubes stiff and strong in nature. Nanotubes exhibit a remarkable electronic and mechanical characteristic, as summarized by Hoenlein *et al.* (2003) in Table 2.1.

Table 2.1 Electrical and mechanical characteristics of carbon nanotubes (Hoenlein *et al.*, 2003).

Electrical Conductivity	Metallic or semiconducting
Electrical Transport	Ballistic, no scattering
Maximum current density	~10^{10} A/cm^2
Maximum strain	0.11% at 1 kV
Thermal Conductivity	6000 W/mK
Diameter	1 to 100 nm
Length	Up to millimeters
Gravimetric surface	>1500 m^2/g
E-modulus	1000 GPa

2.6.1 Bending of CNT with Respect to Mechanical Properties

The strong covalent carbon-carbon bond on the tube structure, initiate the strength tube property which make it stronger than steel (Endo *et al.*, 2004). Noted that the mechanical properties of the nanotubes itself is a challenge to experimentally

study due to the difficulty in obtaining pure CNTs which is free from amorphous, graphitic, and polyhedral carbon particles (Ruoff and Lorents, 1996).

Poncharal *et al.* (1999) has demonstrated that nanotubes can bend to a certain degree when stress is applied and return to its original form after the stress is released. This behavior makes nanotubes special compared to other type of filler due to the susceptibility towards fracture when the tubes are subjected to stress beyond the elastic limit. Moreover, CNT offer ease of processing in composites especially due to the lack of breakdown during processing. This is in contrast with carbon fibers in which the fiber breakdown occurs during composite processing (Schadler *et al.*, 1998).

2.6.2 Electronic Structure and Electron Transport in CNT

The electronic structure of carbon nanotubes can be either metallic or semiconducting depending on the diameter and helicity of the tubes (Saito *et al.*, 1992; Kang *et al.*, 2006). The helicity introduces significant changes in electronic density states which show the electronic character for the nanotubes. The enhanced electronic property enables ballistic transport over more than 100 nm occurs (Bernholc *et al.*, 2002).

Figure 2.10 shows the schematic image on the electron transfer in metal, semiconductor and graphite by Collins and Avouris (2000). As can be seen in Figure 2.10, there are two separate phases that is red and light blue. Red phase indicate the collection of energy states that are pack with electrons, while the light blue phase indicate the empty space for the electron to move in. For metals, the electron can

simply be transferred from the filled energy states (red) to the empty energy states (blue) because there were many electrons that can directly move to the adjacent conduction states. As for semiconductors, additional energy is needed in order to jump across the gaps to the first available conduction states (from red to blue). Finally graphite materials, usually have semimetallic conducting behavior that conduct through minimal point. Applying external boost allowing more electron to access the narrow path to the conduction state.

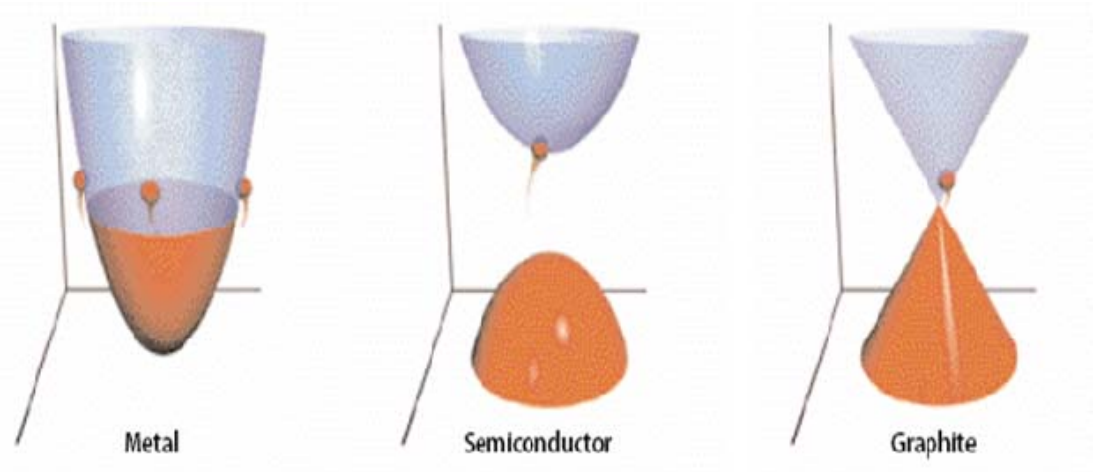

Figure 2.10 Schematic images on electron transfer in metal, semiconductor and graphite in order to determine the electrical properties of the materials (Collins and Avouris, 2000).

Figure 2.11 illustrates the semiconducting and metallic behavior of the straight and twisted nanotubes by Collins and Avouris (2000). For the straight nanotubes (Figure 2.11a), it looks like the graphite sheet (left) was rolled into the center of the tube. The nanotubes geometry limits the electron transfer and makes two thirds of nanotubes metallic while the rest one third is semiconducting. The point at which there is close contact that joins the electron with conduction states is known as Fermi point. For twisted nanotubes (Figure 2.11b), the graphite sheets were rolled into twisted dimension. The twisted nanotube allowed energy states for the electron

to have an incision at an angle resulted in one third of the nanotubes is metallic while the rest is semiconducting.

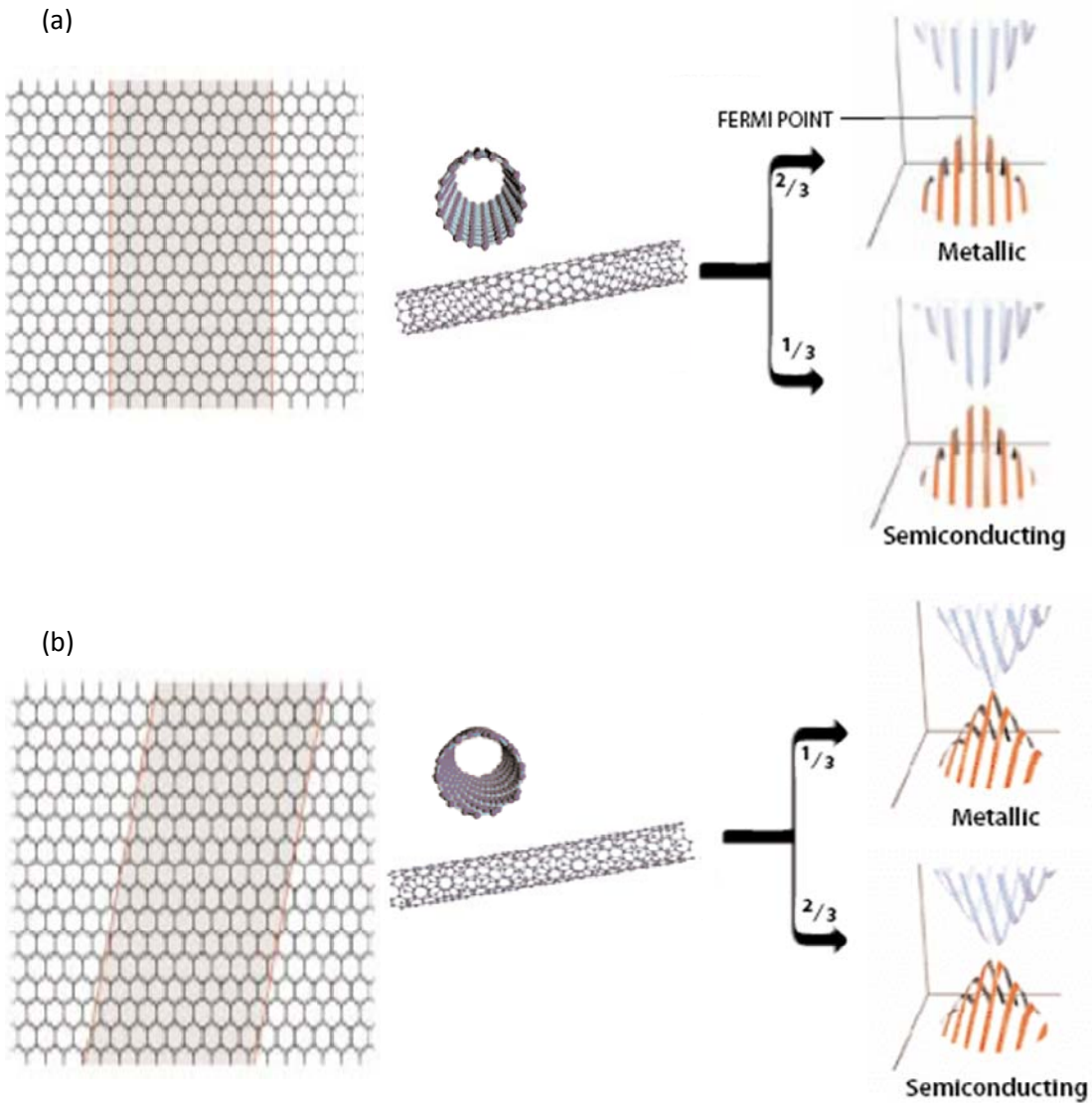

Figure 2.11 Schematic drawing on metallic and semiconducting of (a) straight nanotubes and (b) twisted nanotubes (Collins and Avouris, 2000).

Few facts need to be consider with regard to electron transport in MWCNT, i.e:

a) the semimetallic behavior, which have drastic effect on the band structure and on the scattering mechanism.

b) the effect of reduced dimensionality.

c) impact on weak disorder due to the quantum aspects of conduction.

d) possibility of walls intercalation and its effects.

The MWCNT also can behave as an ultimate fiber while SWCNT can behave as pure quantum wires. It is known, MWCNT has more than one carrier, which were electrons and positive holes. The contribution of each type of carrier is important and should be taken into account (Issi and Charlier, 1999). Due to the one-dimensional electronic structure, the electronic transport in CNT occurs ballistically over the length of the tube which enabling them to carry high currents with essentially no heating (Baughman *et al.*, 2002). The electronic properties of the MWCNT are almost similar to those perfect SWCNT.

2.6.3 Thermal Conductivity Behavior of CNT

Thermal conductivity of MWCNT is~3000W/mK while SWCNT is~6000W/mK. These indicate that CNT have very good thermal conductivity which is greater than diamond and even graphite (~2000W/mK). There are two possible physical mechanisms that contribute to the high thermal conduction of the CNT; i) electron-phonon interactions. This interaction mainly depends on the electronic band structure and the electron scattering process and ii) phonon-phonon interactions. This interaction depends on the vibrational modes of the lattice. At room temperature for semiconductor CNT, the phonon-phonon interaction dominate the thermal conductivity and the electron-phonon interactions only give small contribution due to the large band gap and low density of the free charge carriers. Moreover, thermal conductivity of the nanotube is more sensitive to the states with highest band velocity and the largest mean free path. The thermal conductivity along the tube axis has at least two orders of magnitude larger than normal to the tube axis. Therefore, the

thermal conductivity of SWCNT bundle or isolated MWCNT should be close to their constituents tubes, with some inter-tube thermal conduction that could occur (Sinnott and Aluru, 2006).

Even though Ijima predicted that CNT have very high thermal conductivity among all of carbon materials, the thermal conductivity of the CNT reinforced in polymer composite was low. The individual measurements of MWCNT at room temperature is approximately 3000 W/mK. However, this value was far smaller when the CNT embedded in the polymer matrix due to the interface scattering or defects present on the tube surface (Kumar *et al.*, 2007a; Huxtable *et al.*, 2003).

2.6.3.1 Effects of Different Tube Length and Tubes Chirality on Thermal Conductivity of CNT

Sinnott and Aluru (2006) reviewed effect of tube length variation on the thermal conductivity of the tubes (Figure 2.12). The thermal conductivity of the short tube that is less than few micrometers have ballistic transport features compared to the infinitely long tube. The finite size restricts the phonon motion and causes the thermal conductivity to vary with the nanotube length. In addition, tube with difference chirality and diameter, can have different thermal conductivity properties. They also reported that nanotubes with smaller diameter have radial and azimuthal components that are larger than those tubes with large diameter. For armchair and chiral SWCNT, the σ-bond along the circumferences are strongly strained compared to the zigzag nanotube which could limit the phonon mean free path due to the scattering effect and lower the thermal conductivity. For armchair and zigzag nanotubes, the atom chains are parallel to the tube axis while for chiral nanotubes, the atom chains are in helix position. Therefore, in chiral nanotube position, it is easy

to transfer the momentum in radial direction since axial direction would lower the thermal conductivity of the nanotubes.

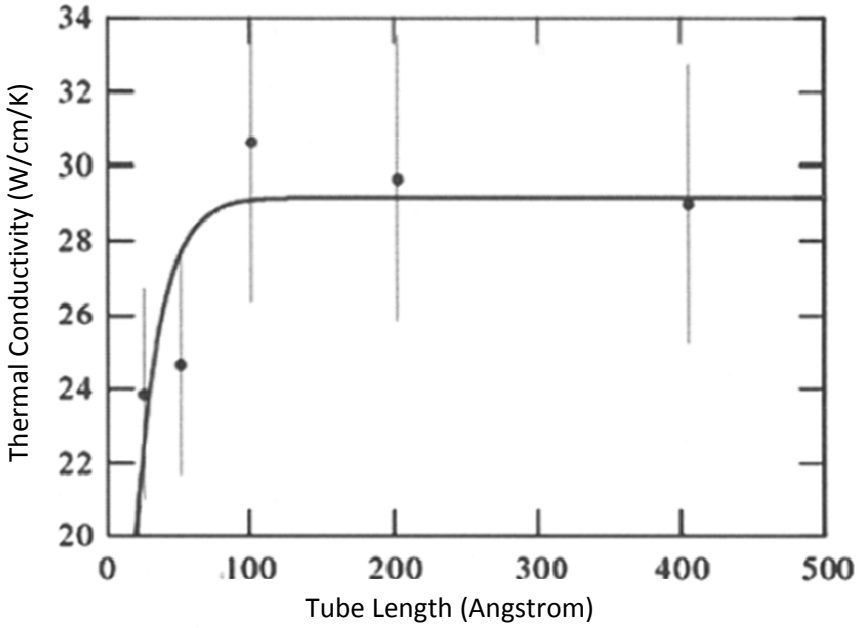

Figure 2.12 Thermal conductivity versus tube length (Sinnott and Aluru, 2006).

2.7 Surface Treatment on CNT

2.7.1 Why Surface Treatment is Important on CNT ?

The as-produced CNT has smooth tube structure. The smooth atomically tube surface with sp^2 hybridized carbon structure has limited ability to form strong bonding with surrounding matrix (Barber *et al.*, 2004). Moreover, the π-π interactions, long and entangled CNT tends to aggregate strongly in bundles. In addition, the tube aggregates together because of their high surface energy and van der Waals attraction between the neighboring tubes. Their long tube length make the processing become hard to control. Thus, CNTs behave as a large macromolecules and making the processing of CNTs in solvent become difficult. In fact, it is an obstacle during preparing CNT nanocomposites and furthermore, it will affect the properties of the nanocomposites produced.

Oxidation treatment on CNT surface creates some functional groups on the tube surface and cause strong interaction with matrix (Lee *et al.*, 2005). This allows the modified CNT to interact with the surrounding matrix via defects create on the nanotube surface or polymer chains wrapping around the nanotube itself. There are many evidences reported by researchers that indicate the presence of functional groups can serves as starting point for binding chemical molecules on the nanotube surfaces with surrounding matrix (Philip *et al.*, 2004; Zhang *et al*., 2004; Zhu *et al*., 2005; Cervini *et al*., 2008; Ma *et al*., 2010a).

2.7.2 Types of Surface Treatment on CNT

There are two main approaches to CNT surface modification. One is covalent attachment while the other is non-covalent attachment. For noncovalent attachment, the CNT was surrounded or wrapped by polymer chain. The advantage in this type of attachment is the nature of the CNT is not altered. The disadvantage of the noncovalent attachment is the interfacial adhesion between CNT and the wrapping polymer molecule might be weak, thus stress transfer efficiency might be low. Figure 2.13 shows the example of non-covalent treatment on CNT by wrapping the hydrolyzed poly(styrene-co-maleic anhydride) (HSMA) on the CNT surface.

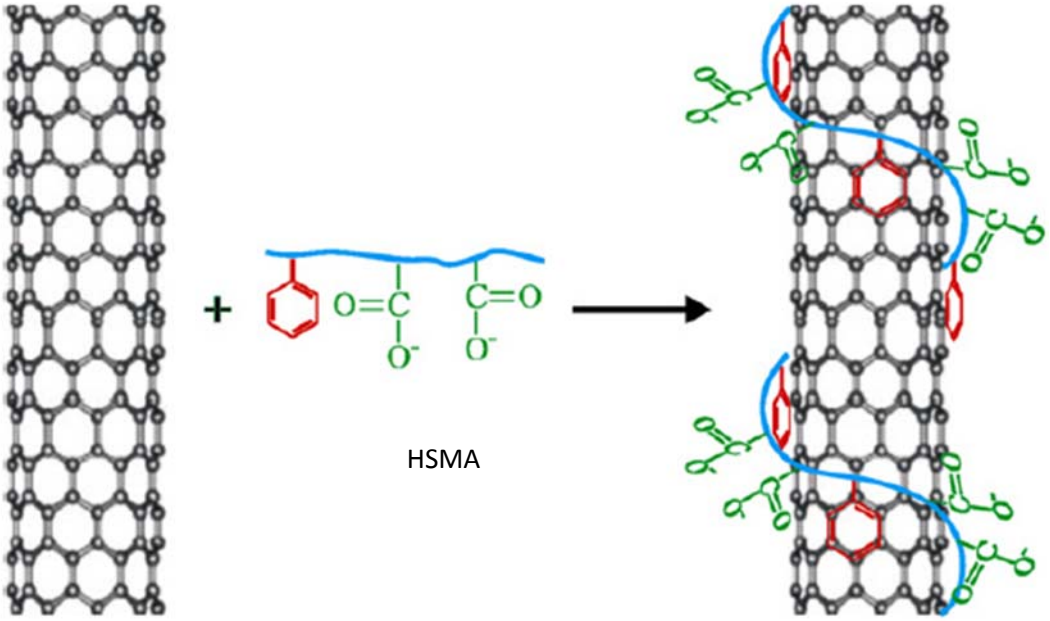

Figure 2.13 Non-covalent treatment of hydrolyzed poly(styrene-co-maleic anhydride) (HSMA) with CNT (Xue *et al.*, 2008).

In comparison the covalent attachment, the functional groups is created on the CNT surface, which can improve the interfacial adhesion between the CNT surfaces and surround matrix. Moreover, the stress transfer is greatly enhanced due to the good bonding between CNT and polymer. By functionalizing the CNT surfaces, the individual tubes can be separated from the tubes bundle and allow tubes to disperse freely in solvent or polymer. Covalent functionalization can be on either the tube end or sidewall of the nanotubes. Oxidation treatment by strong acids can create defects or functional groups either on the sidewall or at the end of the nanotubes (Figure 2.14).